Intermolecular N—H⋯O Hydrogen Bonding Assisted by Resonance. II. Self Assembly of Hydrogen-Bonded Secondary Enaminones in Supramolecular Catemers†

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Abstract

The crystal structures of 15 compounds containing the 2-en-3-amino-1-one heterodienic system and forming intermolecular N—H⋯O hydrogen bonds assisted by resonance (RAHB) are reported: (1) 3-phenylamino-2-cyclohexen-1-one; (2) 3-(4-methoxyphenylamino)-2-cyclohexen-1-one; (3) 3-(4-chlorophenylamino)-2-cyclohexen-1-one; (4) 3-(4-methoxyphenylamino)-2-methyl-2-cyclohexen-1-one; (5) 3-(4-methoxyphenylamino)-5-methyl-2-cyclohexen-1-one; (6) 3-isopropylamino-5,5-dimethyl-2-cyclohexen-1-one; (7) 3-phenylamino-5,5-dimethyl-2-cyclohexen-1-one; (8) 3-(3-methoxyphenylamino)-5,5-dimethyl-2-cyclohexen-1-one; (9) N,N-3-azapentane-1,5-bis[1-(3-oxo-5,5-dimethyl-1-cyclohexenyl)]; (10) 3-phenylamino-6,6-dimethyl-2-cyclohexen-1-one; (11) 3-(2-methoxyphenylamino)-6,6-dimethyl-2-cyclohexen-1-one; (12) 3-(3-chlorophenylamino)-6,6-dimethyl-2-cyclohexen-1-one; (13) 3-(4-chlorophenylamino)-6,6-dimethyl-2-cyclohexen-1-one; (14) 1-(4-chlorophenyl)-4-(4-chlorophenylamino)-6-methyl-2-pyridone; (15) 3-(4-chlorophenylamino)-5-phenyl-2-cyclopenten-1,4-dione. All compounds form intermolecular N—H⋯O=C hydrogen bonds assisted by resonance connecting the heteroconjugated enaminonic groups in infinite chains. Chain morphologies are analyzed to find out crystal engineering rules able to predict and interpret the crystal packing. Simple secondary enaminones [*i.e.* (1)–(13) together with a number of structures retrieved from the Cambridge Structural Database] are found to form hydrogen bonds having π-delocalizations, as characterized by a C=O bond-length average of 1.239 ± 0.004 Å, and hydrogen-bond strengths, represented by the N⋯O average distance of 2.86 ± 0.05 Å, very similar to those previously found for amides. Enaminones, however, can be easily substituted by chemical groups able to influence both π-conjugations and N⋯O hydrogen-bond distances. Some substituted enaminones, retrieved from the literature, display, in fact, N⋯O hydrogen-bond distances as short as 2.627 Å and large π-delocalizations with C=O double-bond distances as long as 1.285 Å. These effects appear to be associated with (a) the presence of further π-conjugated systems involving the C=O and NH groups of the enaminone

moiety or (b) the transformation of the enaminone carbonyl group in an amidic function.

1. Introduction

Intermolecular N—H⋯O=C hydrogen bonding has been mainly studied in crystals of compounds containing the amide moiety (Jeffrey & Saenger, 1991; Berkovitch-Yellin & Leiserowitz, 1980; Leiserowitz & Tuval, 1978; Dauber & Hagler, 1980; Görbitz, 1989). Amides are, in fact, the simplest functional groups able to give N—H⋯O=C resonant hydrogen-bonded chains which are essential for determining peptide and protein conformations, and molecular association in crystals, and, for these reasons, are of great importance in molecular recognition studies and in the planning of crystalline materials displaying new physical and chemical properties (Klebe, 1994; Baker & Hubbard, 1984; Hollingsworth & Ward, 1994; MacDonald & Whitesides, 1994; Whitesides *et al.*, 1991; Lewis *et al.*, 1996). In a previous paper (Bertolasi *et al.*, 1995) it has been shown that structural aggregates analogous to amide chains are also produced by other heteroconjugated systems such as enaminones HN—C=C—C=O, which are strictly related to the well known β-diketone enol moiety HO—C=C—C=O (Gilli *et al.*, 1993; Bertolasi *et al.*, 1996) and, likewise, are found to form easily either intramolecular (I) or intermolecular (II) resonance-assisted hydrogen bonds [RAHB (Gilli *et al.*, 1989; Gilli *et al.*, 1994; Gilli *et al.*, 1996)]. When the resonant system is embedded in a cycle [see for instance (IIIa), (b) and (c)], the formation of the intramolecular hydrogen bond is forbidden and the C=O and N—H groups can only be engaged in intermolecular
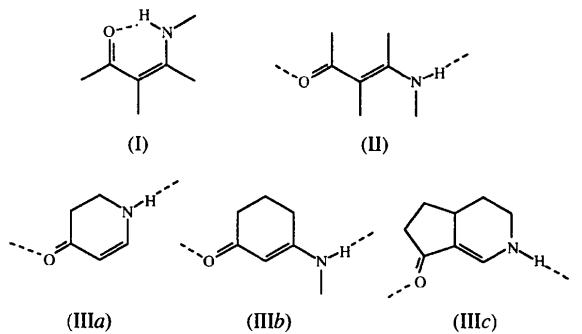
(I)   (II)

(IIIa)   (IIIb)   (IIIc)

bonds which give rise, in the crystal, to infinite molecular chains of various topologies. In order to study the metric and morphology of these hydrogen-bonded chains a series of 15 secondary enaminones, whose chemical formulae are shown in Fig. 1, have been synthesized and submitted to crystal structure analysis. Compounds (1)–(13) are simple secondary enaminones (3-amino-2-cyclohexen-1-one derivatives), which do not carry any substituents which can influence the π-conjugation within the heterodiene, while two others, (14) and (15), are the strictly related 4-amino-2-pyridone and 3-amino-2-cyclopenten-1,4-dione derivatives. Experimental findings are compared with the literature data retrieved from CSD files (Allen et al., 1979) in order to discover which compounds containing the enaminone moiety are able to produce the shortest N···O intermolecular distances. It will be shown that enaminones can represent a useful group to be employed as an alternative to amides in order to aggregate molecules in catemers by means of

(1)
(2) 4'-OMe
(3) 4'-Cl
(4) 2-Me-4'-OMe
(5) 5-Me-4'-OMe
(7) 5,5-di-Me
(8) 5,5-di-Me-3'-OMe
(10) 6,6-di-Me
(11) 6,6-di-Me-2'-OMe
(12) 6,6-di-Me-3'-Cl
(13) 6,6-di-Me-4'-Cl
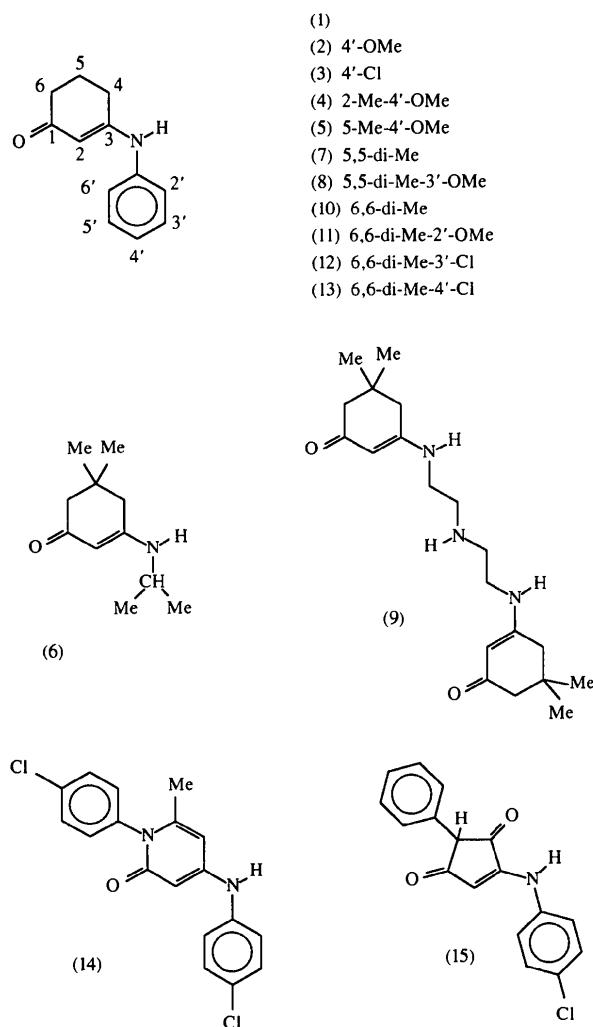
Fig. 1. Chemical formulae of (1)–(15) whose crystal structures have been determined in the present paper.

intermolecular NH···O=C hydrogen bonds, and that the presence of particular substituents at the enaminone fragment is a necessary condition for the formation of strong hydrogen bonds.

2. Experimental

The compounds were synthesized by adding 0.5 mmol [0.25 mmol for (9)] of a primary amine or aniline derivative together with anhydrous $MgSO_4$ to 0.5 mmol of a cyclohexane-1,3-dione derivative [4-hydroxy-6-methyl-2-pyrone for (14) and 4-hydroxy-5-phenyl-4-cyclopenten-1,3-dione for (15)] dissolved in 50 ml of methanol. The solution was refluxed for $\sim$ 1–2 h. After evaporation of the solvent the solid residue was poured in $CHCl_3$ and extracted with ethylic ether. This solution was filtered and dried. The solid residues of (1)–(13) were crystallized using a mixture of ethylic ether and methanol and those of (14) and (15) from acetonitrile. At variance with (1)–(13) and (15), (14) is the result of a double nucleophilic attack to both the hydroxyl group and the oxygen inside the pyrone ring.

Crystal data, data collection and refinement details are given in Table 1.† All intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from Cromer & Waber (1974). Structures were solved by direct methods using the SIR88 (Burla et al., 1989) system of programs and all other calculations were accomplished using MolEN (Fair, 1990) and PARST (Nardelli, 1983). All structures were refined on F by full-matrix least-squares. For (1), (2), (6), (7), (8), (9), (14) and (15) the refinement was anisotropic for non-H and isotropic for H atoms. In (9) the molecule lies on a twofold axis passing through the N2 atom, then the H(N2) is disordered and refined with 0.5 occupancy. The cyclohexenone C5 atom is disordered in (3), (4) and (5), while C5, C7 and C8 are disordered in (10) (molecule B), (12) and (13) (molecule A). All disordered C atoms were refined over two positions with occupancy 0.5; in this case all the non-H atoms were refined anisotropically and H atoms isotropically, except the H atoms implied in the molecular disorder which were taken in fixed calculated positions with their appropriate occupancies. For (13) also the H atoms bonded to the nondisordered C7B and C8B atoms were taken in fixed calculated positions.

3. Results and discussion

Final coordinates are given in Table 2 and a selection of bond distances and angles in Table 3. ORTEP (Johnson,

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_{12}H_{13}NO$	$C_{13}H_{15}NO_2$	$C_{12}H_{12}ClNO$	$C_{14}H_{17}NO_2$	$C_{14}H_{17}NO_2$
Chemical formula weight	187.24	217.27	221.69	231.29	231.29
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	6.112 (3)	5.226 (2)	5.908 (1)	7.079 (1)	5.604 (1)
b (Å)	11.173 (1)	14.047 (2)	13.583 (1)	15.996 (3)	13.667 (2)
c (Å)	14.428 (2)	16.134 (2)	14.058 (2)	11.231 (3)	16.742 (3)
β (°)	90.79 (3)	96.48 (2)	96.18 (2)	92.78 (2)	95.02 (1)
V (Å³)	985.2 (5)	1176.8 (5)	1121.6 (3)	1270.2 (4)	1277.3 (4)
Z	4	4	4	4	4
D_x (Mg m⁻³)	1.2624	1.2263	1.3129	1.2094	1.2027
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10–15	10–15	10–15	10–15	10–15
μ (mm⁻¹)	0.0805	0.0828	0.3123	0.0807	0.0802
Temperature (K)	295	295	295	295	295
Crystal form	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic
Crystal size (mm)	0.48 × 0.26 × 0.14	0.45 × 0.29 × 0.17	0.52 × 0.24 × 0.08	0.57 × 0.48 × 0.36	0.40 × 0.24 × 0.13
Crystal color	Pale yellow	Pale yellow	Colorless	Yellow	Colorless
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None	None	None
No. of measured reflections	2448	2921	2805	3287	2860
No. of independent reflections	2359	2832	2702	3053	2771
No. of observed reflections	1508	1471	1445	2141	1109
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.008	0.020	0.018	0.013	0.034
θ_{max} (°)	28	28	28	28	27
Range of h, k, l	$-8 \rightarrow h \rightarrow 8$ $0 \rightarrow k \rightarrow 14$ $0 \rightarrow l \rightarrow 19$	$-6 \rightarrow h \rightarrow 6$ $0 \rightarrow k \rightarrow 18$ $0 \rightarrow l \rightarrow 21$	$-7 \rightarrow h \rightarrow 7$ $-17 \rightarrow k \rightarrow 0$ $0 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 21$ $-14 \rightarrow l \rightarrow 14$	$-7 \rightarrow h \rightarrow 7$ $0 \rightarrow k \rightarrow 17$ $0 \rightarrow l \rightarrow 21$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections (min)	120	120	120	120	120
Intensity decay (%)	None	None	None	None	None
Refinement					
Refinement on	F	F	F	F	F
R	0.046	0.048	0.042	0.051	0.052
wR	0.062	0.056	0.047	0.079	0.063
S	2.02	2.07	1.72	2.36	1.84
No. of reflections used in refinement	1508	1471	1445	2141	1109
No. of parameters used	179	205	185	207	199
H-atom treatment	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic
Weighting scheme	$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.03F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.03F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.05F2)^2]$	$w = 4F^2/[\sigma(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{max}$	0.01	0.01	0.03	0.03	0.03
$\Delta\rho_{max}$ (e Å⁻³)	0.43	0.16	0.15	0.18	0.22
$\Delta\rho_{min}$ (e Å⁻³)	−0.24	−0.12	−0.12	−0.14	−0.19
Extinction method	None	None	None	None	None
Source of atomic scattering factors	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)

Table 1 (cont.)

	(6)	(7)	(8)	(9)	(10)
Crystal data					
Chemical formula	$C_{11}H_{19}NO$	$C_{14}H_{17}NO$	$C_{15}H_{19}NO_2$	$C_{20}H_{33}N_3O_2$	$C_{14}H_{17}NO$
Chemical formula weight	181.28	215.29	245.32	347.50	215.29
Cell setting	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$Pna2_1$	$C2/c$	$P\bar{1}$
a (Å)	7.139 (1)	9.493 (1)	27.458 (4)	31.779 (5)	9.608 (1)
b (Å)	9.080 (4)	13.061 (3)	7.180 (2)	5.714 (1)	11.248 (2)
c (Å)	9.194 (1)	10.305 (1)	14.210 (2)	11.334 (5)	12.096 (4)
α (°)	106.22 (2)		106.38 (2)		
β (°)	92.33 (1)	105.51 (1)		92.76 (3)	91.22 (2)
γ (°)	97.90 (2)		98.91 (1)		
V (Å^3)	564.9 (3)	1231.2 (3)	2801 (1)	2056 (1)	1236.1 (5)
Z	2	4	8	4	4
D_x (Mg m^{-3})	1.0658	1.1615	1.1633	1.1228	1.1569
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10–15	10–15	10–15	10–15	10–15
μ (mm^{-1})	0.0674	0.0727	0.0768	0.0728	0.0724
Temperature (K)	295	295	295	295	295
Crystal form	Prismatic	Prismatic	Prismatic	Plated	Prismatic
Crystal size (mm)	0.55 × 0.24 × 0.19	0.43 × 0.41 × 0.38	0.48 × 0.38 × 0.31	0.48 × 0.29 × 0.07	0.48 × 0.33 × 0.26
Crystal color	Colorless	Colorless	Yellow	Pale yellow	Colorless
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None	None	None
No. of measured reflections	2886	3118	3505	2529	6290
No. of independent reflections	2717	2964	3505	2487	5941
No. of observed reflections	1677	1942	2351	1115	2958
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.016	0.022	–	0.023	0.019
θ_{max} (°)	28	28	28	28	28
Range of h, k, l	$-9 \rightarrow h \rightarrow 9$ $-12 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 12$	$-12 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 17$ $0 \rightarrow l \rightarrow 13$	$0 \rightarrow h \rightarrow 36$ $0 \rightarrow k \rightarrow 9$ $0 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 42$ $0 \rightarrow k \rightarrow 7$ $-15 \rightarrow l \rightarrow 15$	$0 \rightarrow h \rightarrow 12$ $-14 \rightarrow k \rightarrow 14$ $-16 \rightarrow l \rightarrow 16$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections (min)	120	120	120	120	120
Intensity decay (%)	None	None	None	None	None
Refinement					
Refinement on	F	F	F	F	F
R	0.041	0.040	0.040	0.045	0.058
wR	0.052	0.054	0.044	0.052	0.070
S	1.72	2.14	1.42	1.62	1.93
No. of reflections used in refinement	1677	1942	2351	2487	2958
No. of parameters used	194	214	476	182	412
H-atom treatment	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic
Weighting scheme	$w = 4 F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.03F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4 F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.05F^2)^2]$
$(\Delta/\sigma)_{max}$	0.01	0.03	0.02	0.02	0.02
$\Delta\rho_{max}$ (e Å^{-3})	0.15	0.15	0.11	0.07	0.43
$\Delta\rho_{min}$ (e Å^{-3})	−0.12	−0.10	−0.10	−0.11	−0.30
Extinction method	None	None	None	None	None
Source of atomic scattering factors	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)

Table 1 (*cont.*)

	(11)	(12)	(13)	(14)	(15)
Crystal data					
Chemical formula	$C_{15}H_{19}NO_2$	$C_{14}H_{16}ClNO$	$C_{14}H_{16}ClNO$	$C_{18}H_{14}Cl_2N_2O$	$C_{17}H_{12}ClNO_2$
Chemical formula weight	245.32	249.74	249.74	345.23	297.74
Cell setting	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$Pbca$	$P2_1$	$P\bar{1}$	$Pbca$	$P2_1$
a (Å)	10.546 (1)	7.313 (1)	9.756 (3)	14.244 (2)	7.075 (2)
b (Å)	14.205 (4)	11.778 (1)	11.983 (2)	9.645 (1)	13.332 (2)
c (Å)	18.323 (2)	8.017 (1)	12.043 (1)	23.711 (3)	15.030 (2)
α (°)		101.53 (1)			
β (°)			107.26 (1)	91.99 (2)	95.17 (2)
γ (°)		98.83 (2)			
V (Å^3)	2744.9 (9)	659.4 (1)	1360.0 (5)	3257.5 (7)	1411.9 (5)
Z	8	2	4	8	4
D_x (Mg m^{-3})	1.1873	1.2578	1.2197	1.4079	1.4007
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10–15	10–15	10–15	10–15	10–15
μ (mm^{-1})	0.0784	0.2733	0.2650	0.4036	0.2736
Temperature (K)	295	295	295	295	295
Crystal form	Prismatic	Prismatic	Prismatic	Prismatic	Plated
Crystal size (mm)	0.60 × 0.36 × 0.19	0.50 × 0.35 × 0.15	0.45 × 0.25 × 0.20	0.70 × 0.25 × 0.15	0.53 × 0.48 × 0.05
Crystal color	Colorless	Colorless	Colorless	Pale yellow	Yellow
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None	None	None
No. of measured reflections	3297	2134	6292	3542	3174
No. of independent reflections	3297	2010	5936	3542	3064
No. of observed reflections	1940	1453	2928	1837	1554
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	–	0.010	0.012	–	0.017
θ_{max} (°)	28	30	27	27	27
Range of h, k, l	$0 \rightarrow h \rightarrow 13$	$-10 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 18$	$-9 \rightarrow h \rightarrow 9$
	$0 \rightarrow k \rightarrow 18$	$0 \rightarrow k \rightarrow 16$	$-15 \rightarrow k \rightarrow 15$	$0 \rightarrow k \rightarrow 12$	$0 \rightarrow k \rightarrow 17$
	$0 \rightarrow l \rightarrow 24$	$0 \rightarrow l \rightarrow 11$	$-15 \rightarrow l \rightarrow 15$	$0 \rightarrow l \rightarrow 30$	$0 \rightarrow l \rightarrow 19$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections (min)	120	120	120	120	120
Intensity decay (%)	None	None	None	None	None
Refinement					
Refinement on	F	F	F	F	F
R	0.047	0.044	0.048	0.041	0.042
wR	0.055	0.060	0.060	0.047	0.047
S	1.77	1.70	1.84	1.64	1.60
No. of reflections used in refinement	1940	1453	2928	1837	1554
No. of parameters used	239	200	398	264	238
H-atom treatment	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic	H atoms isotropic
Weighting scheme	$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.05F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$	$w = 4F^2/[\sigma^2(I) + (0.03F^2)^2]$
$(\Delta/\sigma)_{max}$	0.01	0.02	0.01	0.02	0.01
$\Delta\rho_{max}$ (e Å^{-3})	0.17	0.24	0.29	0.26	0.17
$\Delta\rho_{min}$ (e Å^{-3})	−0.12	−0.18	−0.23	−0.21	−0.14
Extinction method	None	None	None	None	None
Source of atomic scattering factors	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)	Cromer & Waber (1974)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(Å^2)$

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta^{ij}\mathbf{a}_i.\mathbf{a}_j.$

Table 2 (*cont.*)

	x	y	z	B_{eq}/B
(1)				
O1	0.5038 (3)	0.3149 (1)	0.61820 (9)	0.0687 (5)
N1	0.3886 (2)	0.1846 (1)	0.30902 (9)	0.0455 (4)
C1	0.5582 (3)	0.3129 (2)	0.5357 (1)	0.0444 (5)
C2	0.4447 (3)	0.2435 (2)	0.4685 (1)	0.0435 (5)
C3	0.4926 (3)	0.2481 (2)	0.3761 (1)	0.0384 (5)
C4	0.6660 (3)	0.3313 (2)	0.3428 (1)	0.0499 (6)
C5	0.8451 (4)	0.3462 (2)	0.4139 (1)	0.0602 (6)
C6	0.7521 (3)	0.3855 (2)	0.5062 (1)	0.0513 (6)
C7	0.2205 (3)	0.0989 (2)	0.3201 (1)	0.0395 (5)
C8	0.0389 (3)	0.1043 (2)	0.2611 (1)	0.0480 (6)
C9	-0.1278 (3)	0.0228 (2)	0.2696 (1)	0.0550 (6)
C10	-0.1185 (4)	-0.0645 (2)	0.3359 (1)	0.0560 (6)
C11	0.0648 (4)	-0.0725 (2)	0.3934 (1)	0.0579 (7)
C12	0.2340 (3)	0.0078 (2)	0.3854 (1)	0.0491 (6)
(2)				
O1	0.6382 (3)	0.5967 (1)	0.7979 (1)	0.0683 (6)
N1	0.6528 (4)	0.2844 (1)	0.6921 (1)	0.0542 (6)
O2	-0.0825 (3)	0.3140 (1)	0.4165 (1)	0.0713 (5)
C1	0.7269 (5)	0.5145 (1)	0.8019 (1)	0.0528 (7)
C2	0.6329 (4)	0.4422 (1)	0.7457 (1)	0.0506 (7)
C3	0.7333 (4)	0.3526 (1)	0.7472 (1)	0.0474 (6)
C4	0.9497 (5)	0.3248 (2)	0.8111 (2)	0.0654 (8)
C5	0.9773 (7)	0.3884 (2)	0.8847 (2)	0.0956 (11)
C6	0.9521 (6)	0.4907 (2)	0.8646 (2)	0.0828 (11)
C7	0.4661 (4)	0.2959 (1)	0.6213 (1)	0.0483 (7)
C8	0.4969 (4)	0.3623 (1)	0.5603 (1)	0.0552 (7)
C9	0.3175 (5)	0.3713 (1)	0.4913 (1)	0.0566 (8)
C10	0.1055 (4)	0.3121 (2)	0.4825 (1)	0.0528 (7)
C11	0.0768 (5)	0.2444 (2)	0.5429 (1)	0.0582 (7)
C12	0.2559 (5)	0.2363 (2)	0.6117 (1)	0.0542 (7)
C13	-0.0813 (6)	0.3903 (2)	0.3594 (2)	0.0800 (10)
(3)				
Cl1	0.1867 (1)	0.13486 (5)	0.64218 (5)	0.0760 (2)
O1	-0.5641 (4)	-0.3249 (2)	0.3875 (1)	0.0963 (8)
N1	-0.4456 (3)	-0.1915 (1)	0.6987 (1)	0.0534 (6)
C1	-0.6077 (5)	-0.3220 (2)	0.4717 (2)	0.0639 (8)
C2	-0.4984 (4)	-0.2566 (2)	0.5396 (1)	0.0533 (7)
C3	-0.5439 (4)	-0.2540 (2)	0.6325 (1)	0.0458 (6)
C4	-0.7125 (5)	-0.3241 (2)	0.6674 (2)	0.0623 (8)
C5	-0.7415 (11)	-0.4140 (4)	0.6065 (4)	0.0787 (19)
C5'	-0.8865 (10)	-0.3569 (4)	0.5931 (4)	0.0781 (21)
C6	-0.7837 (6)	-0.3906 (2)	0.5033 (2)	0.0869 (12)
C7	-0.2912 (4)	-0.1151 (2)	0.6825 (1)	0.0455 (6)
C8	-0.3536 (4)	-0.0405 (2)	0.6183 (2)	0.0558 (8)
C9	-0.2051 (5)	0.0349 (2)	0.6052 (2)	0.0594 (8)
C10	0.0038 (4)	0.0366 (2)	0.6574 (2)	0.0516 (7)
C11	0.0687 (4)	-0.0361 (2)	0.7224 (2)	0.0586 (8)
C12	-0.0803 (4)	-0.1121 (2)	0.7346 (2)	0.0549 (7)
(4)				
O1	-0.0645 (2)	0.23020 (9)	0.4985 (1)	0.0641 (4)
O2	1.0123 (2)	0.56264 (9)	0.8675 (1)	0.0644 (4)
N1	0.4063 (2)	0.34976 (9)	0.7578 (1)	0.0496 (4)
C1	0.0639 (2)	0.2816 (1)	0.5192 (1)	0.0482 (5)
C2	0.1641 (2)	0.2871 (1)	0.6332 (1)	0.0402 (4)
C3	0.3076 (2)	0.3441 (1)	0.6519 (1)	0.0414 (4)
C4	0.3616 (3)	0.4042 (1)	0.5577 (2)	0.0692 (6)
C5	0.2929 (7)	0.3832 (3)	0.4390 (3)	0.0791 (15)
C5'	0.2106 (6)	0.4171 (3)	0.4639 (3)	0.0683 (14)
C6	0.1174 (4)	0.3403 (2)	0.4220 (2)	0.0833 (8)
C7	0.1128 (3)	0.2277 (1)	0.7291 (2)	0.0549 (5)
C8	0.5586 (2)	0.4067 (1)	0.7839 (1)	0.0435 (5)
C9	0.7403 (3)	0.3885 (1)	0.7499 (2)	0.0557 (5)
C10	0.8870 (2)	0.4420 (1)	0.7788 (2)	0.0571 (6)
C11	0.8560 (2)	0.5147 (1)	0.8419 (1)	0.0459 (5)
C12	0.6759 (2)	0.5342 (1)	0.8742 (2)	0.0467 (5)
C13	0.5281 (2)	0.4796 (1)	0.8447 (2)	0.0471 (5)
C14	0.9873 (3)	0.6362 (1)	0.9355 (2)	0.0758 (7)
(5)				
O1	-0.0649 (5)	0.1163 (2)	0.2217 (2)	0.0675 (9)
O2	0.5311 (5)	-0.1916 (2)	0.5732 (2)	0.0832 (10)
N1	-0.1723 (5)	-0.2035 (2)	0.3174 (2)	0.0588 (10)
C1	-0.1644 (6)	0.0347 (2)	0.2162 (2)	0.0532 (11)
C2	-0.1038 (6)	-0.0427 (2)	0.2702 (2)	0.0503 (11)
C3	-0.2228 (6)	-0.1298 (2)	0.2656 (2)	0.0480 (11)
C4	-0.4203 (7)	-0.1494 (2)	0.2017 (2)	0.0642 (13)
C5	-0.4299 (14)	-0.0853 (5)	0.1325 (4)	0.0560 (25)
C5'	-0.5178 (13)	-0.0586 (5)	0.1615 (4)	0.0557 (27)
C6	-0.3604 (8)	0.0171 (3)	0.1510 (3)	0.0848 (18)
C7	-0.6720 (9)	-0.0891 (4)	0.0823 (3)	0.0966 (17)
C8	0.0030 (6)	-0.1990 (2)	0.3846 (2)	0.0495 (12)
C9	-0.0293 (7)	-0.1414 (3)	0.4494 (2)	0.0600 (13)
C10	0.1413 (7)	-0.1364 (3)	0.5139 (2)	0.0613 (13)
C11	0.3473 (7)	-0.1906 (3)	0.5140 (2)	0.0571 (12)
C12	0.3789 (7)	-0.2510 (3)	0.4490 (2)	0.0657 (13)
C13	0.2088 (7)	-0.2546 (3)	0.3843 (2)	0.0587 (13)
C14	0.5279 (8)	-0.1236 (4)	0.6354 (3)	0.0923 (18)
(6)				
O1	0.2289 (1)	0.2747 (1)	0.0412 (1)	0.0761 (5)
N1	0.8427 (1)	0.1811 (1)	-0.0873 (1)	0.0432 (3)
C1	0.4042 (2)	0.3041 (2)	0.0660 (2)	0.0490 (4)
C2	0.5269 (2)	0.2172 (2)	-0.0250 (2)	0.0460 (4)
C3	0.7202 (2)	0.2575 (1)	-0.0025 (1)	0.0375 (4)
C4	0.8080 (2)	0.3993 (2)	0.1201 (2)	0.0445 (4)
C5	0.6891 (2)	0.4387 (2)	0.2564 (2)	0.0462 (4)
C6	0.4876 (2)	0.4410 (2)	0.1959 (2)	0.0497 (4)
C7	0.6885 (2)	0.3184 (2)	0.3433 (2)	0.0658 (6)
C8	0.7733 (3)	0.5984 (2)	0.3600 (2)	0.0751 (7)
C9	0.7920 (2)	0.0467 (2)	-0.2193 (2)	0.0507 (5)
C10	0.7239 (3)	0.0936 (3)	-0.3552 (2)	0.0807 (8)
C11	0.9607 (3)	-0.0367 (2)	-0.2507 (2)	0.0695 (6)
(7)				
O1	0.1717 (1)	0.14568 (7)	0.8340 (1)	0.0729 (4)
N1	0.3579 (1)	0.43483 (8)	1.1035 (1)	0.0516 (4)
C1	0.1705 (2)	0.2386 (1)	0.8579 (1)	0.0495 (4)
C2	0.2726 (2)	0.2845 (1)	0.9698 (1)	0.0478 (4)
C3	0.2701 (1)	0.3869 (1)	0.9962 (1)	0.0439 (4)
C4	0.1594 (2)	0.4558 (1)	0.9055 (1)	0.0538 (4)
C5	0.1010 (2)	0.4166 (1)	0.7620 (1)	0.0487 (4)
C6	0.0552 (2)	0.3053 (1)	0.7695 (1)	0.0547 (5)
C7	0.2182 (2)	0.4235 (1)	0.6865 (2)	0.0633 (6)
C8	-0.0311 (2)	0.4809 (1)	0.6901 (2)	0.0778 (7)
C9	0.4651 (1)	0.3884 (1)	1.2104 (1)	0.0458 (4)
C10	0.5733 (2)	0.3277 (1)	1.1854 (1)	0.0587 (5)
C11	0.6765 (2)	0.2849 (1)	1.2912 (2)	0.0779 (7)
C12	0.6733 (2)	0.3029 (1)	1.4216 (2)	0.0786 (6)
C13	0.5667 (2)	0.3647 (1)	1.4462 (1)	0.0715 (6)
C14	0.4620 (2)	0.4077 (1)	1.3415 (1)	0.0562 (5)
(8)				
O1A	0.14867 (9)	-0.1796 (3)	0.00000 (0)	0.1165 (12)
O2A	0.31790 (7)	0.2800 (3)	-0.2272 (2)	0.0777 (8)
N1A	0.18364 (7)	0.4631 (3)	-0.0222 (2)	0.0492 (6)
C1A	0.1356 (1)	-0.0158 (4)	-0.0008 (2)	0.0652 (10)
C2A	0.16931 (9)	0.1324 (3)	-0.0142 (2)	0.0523 (8)
C3A	0.15481 (8)	0.3130 (3)	-0.0098 (2)	0.0409 (7)
C4A	0.10273 (9)	0.3617 (3)	0.0109 (2)	0.0472 (7)
C5A	0.07400 (9)	0.2123 (3)	0.0622 (2)	0.0479 (8)
C6A	0.0829 (1)	0.0293 (4)	0.0111 (2)	0.0630 (10)
C7A	0.0913 (1)	0.1982 (5)	0.1638 (2)	0.0769 (13)
C8A	0.0198 (1)	0.2606 (4)	0.0611 (3)	0.0702 (10)
C9A	0.23185 (8)	0.4772 (3)	-0.0564 (2)	0.0466 (8)

Table 2 (*cont.*) Table 2 (*cont.*)

	x	y	z	B_{eq}/B		x	y	z	B_{eq}/B
C10A	0.25054 (9)	0.3561 (4)	−0.1237 (2)	0.0498 (8)	C8B'	0.9273 (7)	0.1680 (5)	0.0839 (5)	0.0804 (22)
C11A	0.29684 (9)	0.3874 (4)	−0.1598 (2)	0.0560 (9)	C9B	0.6373 (3)	0.6837 (2)	0.1509 (2)	0.0561 (8)
C12A	0.3242 (1)	0.5360 (5)	−0.1281 (2)	0.0661 (10)	C10B	0.6661 (3)	0.8064 (3)	0.1461 (2)	0.0766 (10)
C13A	0.3053 (1)	0.6545 (4)	−0.0633 (3)	0.0700 (9)	C11B	0.6174 (4)	0.8996 (3)	0.2292 (3)	0.0946 (13)
C14A	0.2596 (1)	0.6277 (4)	−0.0269 (2)	0.0601 (9)	C12B	0.5401 (4)	0.8728 (3)	0.3155 (3)	0.0835 (13)
C15A	0.2924 (1)	0.1223 (6)	−0.2599 (3)	0.0972 (14)	C13B	0.5106 (3)	0.7512 (3)	0.3201 (2)	0.0710 (10)
O1B	0.09634 (8)	1.1139 (2)	−0.2665 (2)	0.0895 (9)	C14B	0.5587 (3)	0.6565 (2)	0.2381 (2)	0.0633 (9)
O2B	−0.07748 (7)	0.6859 (3)	−0.0457 (2)	0.0741 (7)	(11)				
N1B	0.06178 (7)	0.4727 (3)	−0.2289 (2)	0.0479 (6)	O1	0.2561 (1)	−0.29143 (9)	0.09951 (8)	0.0542 (5)
C1B	0.1098 (1)	0.9500 (3)	−0.2639 (2)	0.0532 (8)	O2	0.0309 (1)	0.1363 (1)	0.21871 (7)	0.0519 (4)
C2B	0.07679 (9)	0.8033 (3)	−0.2440 (2)	0.0461 (7)	N1	0.1136 (1)	0.02444 (9)	0.11447 (9)	0.0376 (4)
C3B	0.09122 (8)	0.6223 (3)	−0.2446 (2)	0.0405 (7)	C1	0.2739 (2)	−0.2065 (1)	0.0872 (1)	0.0344 (5)
C4B	0.14295 (9)	0.5713 (3)	−0.2640 (2)	0.0467 (7)	C2	0.1826 (2)	−0.1374 (1)	0.1084 (1)	0.0366 (5)
C5B	0.16998 (9)	0.7113 (3)	−0.3256 (2)	0.0465 (8)	C3	0.1999 (2)	−0.0434 (1)	0.09895 (9)	0.0317 (5)
C6B	0.1618 (1)	0.9026 (4)	−0.2827 (2)	0.0558 (9)	C4	0.3220 (2)	−0.0061 (1)	0.0686 (1)	0.0410 (5)
C7B	0.1496 (1)	0.7045 (5)	−0.4253 (2)	0.0735 (11)	C5	0.4283 (2)	−0.0772 (1)	0.0756 (1)	0.0398 (5)
C8B	0.2241 (1)	0.6664 (5)	−0.3271 (3)	0.0769 (11)	C6	0.3916 (2)	−0.1743 (1)	0.0458 (1)	0.0359 (5)
C9B	0.01253 (9)	0.4669 (3)	−0.2012 (2)	0.0446 (7)	C7	0.5022 (2)	−0.2423 (1)	0.0566 (1)	0.0540 (7)
C10B	−0.00690 (9)	0.5900 (3)	−0.1361 (2)	0.0461 (7)	C8	0.3580 (2)	−0.1691 (2)	−0.0349 (1)	0.0608 (7)
C11B	−0.05488 (9)	0.5712 (4)	−0.1088 (2)	0.0520 (8)	C9	−0.0115 (2)	0.0112 (1)	0.1403 (1)	0.0356 (5)
C12B	−0.08323 (9)	0.4308 (4)	−0.1446 (2)	0.0616 (10)	C10	−0.0552 (2)	0.0714 (1)	0.1954 (1)	0.0403 (6)
C13B	−0.0637 (1)	0.3081 (4)	−0.2081 (3)	0.0708 (10)	C11	−0.1778 (2)	0.0619 (2)	0.2216 (1)	0.0558 (7)
C14B	−0.0160 (1)	0.3245 (4)	−0.2369 (2)	0.0630 (9)	C12	−0.2557 (2)	−0.0068 (2)	0.1937 (1)	0.0651 (8)
C15B	−0.0506 (1)	0.8338 (6)	−0.0069 (3)	0.0998 (14)	C13	−0.2149 (2)	−0.0648 (2)	0.1391 (1)	0.0608 (7)
(9)					C14	−0.0931 (2)	−0.0551 (1)	0.1121 (1)	0.0486 (6)
O1	−0.11280 (6)	0.3897 (3)	0.6450 (1)	0.0724 (6)	C15	−0.0108 (3)	0.2069 (2)	0.2685 (1)	0.0795 (9)
N1	−0.08048 (5)	−0.1584 (4)	0.3521 (1)	0.0497 (6)	(12)				
N2	0.00000 (0)	−0.2936 (6)	0.25000 (0)	0.0641 (9)	C1	0.2212 (1)	0.00000 (0)	0.3295 (1)	0.0903 (3)
C1	−0.11949 (7)	0.2989 (4)	0.5461 (2)	0.0519 (7)	O1	−0.6481 (2)	0.2224 (2)	0.8805 (3)	0.0615 (7)
C2	−0.09529 (7)	0.1126 (4)	0.5040 (2)	0.0515 (7)	N1	−0.0422 (3)	0.1487 (3)	0.7995 (3)	0.0507 (6)
C3	−0.10292 (6)	0.0150 (4)	0.3948 (2)	0.0436 (6)	C1	−0.4716 (3)	0.2311 (2)	0.9331 (3)	0.0424 (7)
C4	−0.13782 (7)	0.1060 (4)	0.3142 (2)	0.0495 (7)	C2	−0.3557 (3)	0.1848 (2)	0.8329 (4)	0.0454 (7)
C5	−0.17382 (6)	0.2174 (4)	0.3790 (2)	0.0467 (7)	C3	−0.1628 (3)	0.1938 (2)	0.8840 (3)	0.0417 (7)
C6	−0.15468 (8)	0.3932 (4)	0.4663 (2)	0.0568 (9)	C4	−0.0607 (4)	0.2594 (3)	1.0443 (4)	0.0582 (9)
C7	−0.19811 (7)	0.0295 (5)	0.4445 (2)	0.0658 (10)	C5	−0.1706 (7)	0.2557 (5)	1.1824 (6)	0.0442 (15)
C8	−0.20371 (8)	0.3400 (5)	0.2906 (2)	0.0694 (9)	C6	−0.3786 (3)	0.2925 (3)	1.1039 (3)	0.0446 (8)
C9	−0.04554 (7)	−0.2744 (5)	0.4153 (2)	0.0592 (9)	C7	−0.4799 (7)	0.2656 (8)	1.2461 (7)	0.0642 (22)
C10	−0.02248 (7)	−0.4309 (5)	0.3351 (2)	0.0610 (8)	C8	−0.3975 (8)	0.4196 (5)	1.0672 (7)	0.0473 (15)
(10)					C5'	−0.1780 (10)	0.3181 (10)	1.1177 (11)	0.1337 (33)
O1A	0.6569 (2)	0.6615 (2)	0.8538 (1)	0.0734 (7)	C7'	−0.4813 (17)	0.4028 (9)	1.0958 (14)	0.1207 (45)
N1A	0.8242 (2)	0.4135 (2)	0.5157 (1)	0.0513 (6)	C8'	−0.4074 (21)	0.2238 (12)	1.2367 (12)	0.1489 (49)
C1A	0.6912 (3)	0.6484 (2)	0.7537 (2)	0.0495 (7)	C9	−0.0764 (3)	0.0759 (3)	0.6569 (3)	0.0429 (7)
C2A	0.7441 (3)	0.5392 (2)	0.6907 (2)	0.0502 (8)	C10	0.0594 (3)	0.0756 (3)	0.5667 (3)	0.0454 (8)
C3A	0.7774 (2)	0.5181 (2)	0.5788 (2)	0.0458 (7)	C11	0.0419 (4)	0.0016 (3)	0.4329 (3)	0.0526 (8)
C4A	0.7608 (3)	0.6110 (2)	0.5154 (2)	0.0570 (8)	C12	−0.1073 (5)	−0.0733 (3)	0.3793 (4)	0.0634 (10)
C5A	0.7723 (3)	0.7422 (2)	0.5965 (2)	0.0669 (8)	C13	−0.2427 (5)	−0.0729 (3)	0.4690 (5)	0.0646 (10)
C6A	0.6739 (3)	0.7490 (2)	0.6958 (2)	0.0504 (7)	C14	−0.2277 (4)	−0.0005 (3)	0.6056 (4)	0.0563 (8)
C7A	0.5187 (3)	0.7230 (3)	0.6493 (3)	0.0843 (12)	(13)				
C8A	0.7072 (4)	0.8789 (3)	0.7843 (3)	0.0865 (13)	Cl1A	0.0311 (1)	0.45053 (8)	0.8638 (1)	0.1321 (4)
C9A	0.8560 (2)	0.3131 (2)	0.5553 (2)	0.0476 (7)	O1A	0.3653 (2)	−0.1525 (2)	0.7836 (1)	0.0795 (7)
C10A	0.8111 (3)	0.1908 (2)	0.4869 (2)	0.0632 (10)	N1A	0.1766 (2)	0.0559 (2)	0.5392 (2)	0.0593 (7)
C11A	0.8461 (3)	0.0928 (2)	0.5220 (3)	0.0814 (12)	C1A	0.3265 (3)	−0.1457 (2)	0.6865 (2)	0.0564 (8)
C12A	0.9243 (3)	0.1137 (2)	0.6223 (3)	0.0830 (11)	C2A	0.2702 (3)	−0.0492 (2)	0.6658 (2)	0.0540 (8)
C13A	0.9718 (3)	0.2347 (3)	0.6901 (2)	0.0733 (10)	C3A	0.2315 (3)	−0.0348 (2)	0.5611 (2)	0.0509 (8)
C14A	0.9365 (3)	0.3339 (2)	0.6562 (2)	0.0575 (8)	C4A	0.2509 (3)	−0.1230 (2)	0.4582 (2)	0.0666 (9)
O1B	0.8463 (2)	0.3380 (2)	0.2730 (1)	0.0724 (7)	C5A	0.2442 (5)	−0.2394 (4)	0.4873 (4)	0.0604 (18)
N1B	0.6814 (2)	0.5881 (2)	0.0611 (2)	0.0625 (7)	C5A'	0.3469 (7)	−0.2060 (5)	0.4807 (5)	0.0958 (24)
C1B	0.8145 (2)	0.3536 (2)	0.1795 (2)	0.0510 (8)	C6A	0.3404 (3)	−0.2425 (2)	0.5868 (2)	0.0623 (10)
C2B	0.7642 (3)	0.4633 (2)	0.1726 (2)	0.0521 (8)	C7A	0.4983 (5)	−0.2129 (5)	0.5561 (5)	0.0719 (19)
C3B	0.7322 (2)	0.4857 (2)	0.0711 (2)	0.0544 (7)	C7A'	0.4439 (8)	−0.3151 (6)	0.6135 (7)	0.1288 (31)
C4B	0.7534 (3)	0.3944 (2)	−0.0414 (2)	0.0674 (10)	C8A	0.3174 (8)	−0.3546 (5)	0.6225 (6)	0.0962 (27)
C5B	0.7415 (6)	0.2615 (5)	−0.0311 (4)	0.0660 (19)	C8A'	0.1945 (10)	−0.3303 (7)	0.5763 (7)	0.1291 (38)
C5B'	0.8570 (6)	0.3068 (5)	−0.0259 (4)	0.0680 (19)	C9A	0.1418 (3)	0.1489 (2)	0.6184 (2)	0.0514 (8)
C6B	0.8267 (3)	0.2511 (2)	0.0683 (2)	0.0577 (8)	C10A	0.0739 (3)	0.1331 (2)	0.7144 (2)	0.0604 (9)
C7B	0.8041 (9)	0.1258 (6)	0.0864 (6)	0.1066 (33)	C11A	0.0396 (3)	0.2254 (2)	0.7888 (2)	0.0710 (11)
C7B'	0.6689 (7)	0.1667 (5)	0.0424 (5)	0.0804 (23)	C12A	0.0704 (3)	0.3333 (2)	0.7677 (3)	0.0762 (11)
C8B	0.9896 (6)	0.2785 (6)	0.0408 (5)	0.0861 (24)	C13A	0.1340 (4)	0.3507 (2)	0.6710 (3)	0.0832 (12)

Table 2 (cont.)

	x	y	z	B_{eq}/B
C14A	0.1691 (3)	0.2578 (2)	0.5967 (2)	0.0718 (10)
C11B	0.5018 (1)	−0.45460 (8)	1.2114 (1)	0.1215 (4)
O1B	0.1358 (2)	0.1300 (2)	1.3325 (1)	0.0731 (7)
N1B	0.3273 (2)	−0.0783 (2)	1.0188 (2)	0.0662 (8)
C1B	0.1763 (3)	0.1237 (2)	1.2352 (2)	0.0560 (8)
C2B	0.2338 (3)	0.0270 (2)	1.1803 (2)	0.0587 (8)
C3B	0.2742 (2)	0.0134 (2)	1.0724 (2)	0.0555 (9)
C4B	0.2562 (3)	0.1024 (2)	1.0042 (2)	0.0706 (10)
C5B	0.2617 (3)	0.2211 (2)	1.0797 (2)	0.0784 (11)
C6B	0.1586 (3)	0.2194 (2)	1.1729 (2)	0.0584 (9)
C7B	0.1870 (4)	0.3363 (3)	1.2564 (3)	0.0955 (13)
C8B	0.0099 (3)	0.1982 (3)	1.1241 (3)	0.0895 (12)
C9B	0.3649 (3)	−0.1690 (2)	1.0670 (2)	0.0585 (9)
C10B	0.4444 (3)	−0.1455 (2)	1.1695 (2)	0.0621 (10)
C11B	0.4866 (3)	−0.2330 (2)	1.2126 (2)	0.0672 (10)
C12B	0.4497 (3)	−0.3442 (2)	1.1555 (3)	0.0761 (11)
C13B	0.3722 (4)	−0.3692 (3)	1.0528 (3)	0.0918 (14)
C14B (14)	0.3305 (3)	−0.2807 (3)	1.0089 (3)	0.0787 (11)
C11	0.59249 (6)	0.7244 (1)	0.03708 (4)	0.0819 (3)
C12	0.15220 (8)	0.0915 (1)	0.52709 (4)	0.0859 (3)
O1	0.4250 (1)	0.4132 (2)	0.24957 (8)	0.0573 (6)
N1	0.1060 (1)	0.3832 (3)	0.3097 (1)	0.0544 (8)
N2	0.3110 (1)	0.5341 (2)	0.20338 (8)	0.0389 (7)
C1	0.3403 (2)	0.4455 (3)	0.2468 (1)	0.0426 (8)
C2	0.2693 (2)	0.3966 (3)	0.2833 (1)	0.0465 (9)
C3	0.1769 (2)	0.4326 (3)	0.2765 (1)	0.0419 (9)
C4	0.1529 (2)	0.5230 (3)	0.2318 (1)	0.0451 (9)
C5	0.2181 (2)	0.5728 (3)	0.1964 (1)	0.0418 (9)
C6	0.1962 (2)	0.6726 (4)	0.1503 (1)	0.0597 (10)
C7	0.3813 (2)	0.5794 (3)	0.1638 (1)	0.0381 (8)
C8	0.4431 (2)	0.6839 (3)	0.1777 (1)	0.0476 (10)
C9	0.5085 (2)	0.7279 (3)	0.1391 (1)	0.0519 (10)
C10	0.5115 (2)	0.6669 (3)	0.0869 (1)	0.0483 (9)
C11	0.4511 (2)	0.5624 (3)	0.0725 (1)	0.0499 (9)
C12	0.3861 (2)	0.5183 (3)	0.1116 (1)	0.0454 (9)
C13	0.1190 (2)	0.3127 (3)	0.3614 (1)	0.0435 (9)
C14	0.1680 (2)	0.3722 (3)	0.4048 (1)	0.0494 (9)
C15	0.1777 (2)	0.3057 (3)	0.4556 (1)	0.0542 (10)
C16	0.1385 (2)	0.1777 (3)	0.4627 (1)	0.0558 (9)
C17	0.0892 (2)	0.1150 (4)	0.4202 (1)	0.0656 (12)
C18 (15)	0.0802 (2)	0.1831 (4)	0.3692 (1)	0.0604 (11)
C1	0.1243 (2)	0.15359 (7)	0.47484 (5)	0.0898 (4)
O1	−0.3302 (3)	−0.0627 (1)	−0.0908 (1)	0.0674 (7)
O2	−0.3350 (3)	0.2868 (1)	−0.0650 (1)	0.0555 (6)
N1	−0.1645 (3)	0.2174 (2)	0.0980 (1)	0.0436 (7)
C1	−0.3131 (4)	0.0221 (2)	−0.0607 (2)	0.0448 (8)
C2	−0.2151 (4)	0.0521 (2)	0.0220 (2)	0.0458 (8)
C3	−0.2234 (4)	0.1529 (2)	0.0323 (2)	0.0379 (7)
C4	−0.3231 (4)	0.1983 (2)	−0.0501 (2)	0.0410 (8)
C5	−0.4033 (4)	0.1137 (2)	−0.1090 (2)	0.0427 (9)
C6	−0.0898 (4)	0.1981 (2)	0.1872 (2)	0.0425 (9)
C7	−0.0600 (4)	0.2791 (2)	0.2433 (2)	0.0510 (9)
C8	0.0055 (4)	0.2654 (2)	0.3314 (2)	0.0593 (11)
C9	0.0402 (4)	0.1707 (2)	0.3637 (2)	0.0559 (10)
C10	0.0135 (5)	0.0906 (2)	0.3092 (2)	0.0711 (12)
C11	−0.0505 (5)	0.1033 (2)	0.2198 (2)	0.0642 (11)
C12	−0.3793 (4)	0.1183 (2)	−0.2074 (2)	0.0441 (8)
C13	−0.2269 (5)	0.1648 (2)	−0.2400 (2)	0.0629 (11)
C14	−0.2065 (6)	0.1650 (2)	−0.3309 (2)	0.0834 (13)
C15	−0.3356 (7)	0.1184 (3)	−0.3884 (2)	0.0946 (16)
C16	−0.4864 (6)	0.0703 (3)	−0.3574 (2)	0.0916 (15)
C17	−0.5101 (5)	0.0706 (2)	−0.2670 (2)	0.0679 (10)

1976) views of the molecules projected on the mean enaminone plane are shown in Fig. 2, together with the schemes of the hydrogen-bonded catemers observed in the crystal packing; hydrogen-bond parameters are given in Table 4.

3.1. Chain morphologies

All crystals consist of chains of molecules linked by NH$\cdots$O$=$C intermolecular resonant-assisted hydrogen bonds. The hydrogen-bond chain morphologies (Table 5) have been classified according to a double nomenclature already developed for β-diketone enols (Etter *et al.*, 1986; Gilli *et al.*, 1993; Bertolasi *et al.*, 1996). The first is crystallographic; the chain symmetry being described by the symmetry operator relating adjacent molecules in the chain. Symbols *g* for glide, 2_1 for binary screw axis and *t* for lattice translation are used; multiple asymmetric units are indicated as *A–B*, the notation *t*(*A–B*) denoting two interlinked molecules that propagate the chain by simple translation; the prefix pseudo may be used for approximate (*i.e.* noncrystallographic) symmetries, for instance pseudo-2_1. The second notation system defines the hydrogen-bonded chain stereochemistry around the C$=$O and C—N bonds. It follows the (*syn/anti-SYN/ANTI*) nomenclature (Fig. 3) originally proposed by Etter *et al.* (1986) preceded by the value of the C—N(H)$\cdots$O$=$C torsion angle (φ-tors) expressed according to the Klyne & Prelog (1960) convention, for which *sp* = synperiplanar, *sc* = synclinal, *ac* = anticlinal and *ap* = antiperiplanar indicate torsion angles in the range $\pm 30°$, $\pm(30–90)°$, $\pm(90–150)$ and 150–210°, respectively. Finally, other parameters used to describe the chain morphology are φ-plane, which is the angle between the least-squares plane through the O1—C1—C2—C3—N1 atoms of two adjacent monomers, and the C$=$O$\cdots$H angle (θ) and its associated C—C$=$O$\cdots$H torsion angle (θ-tors), which both define the method of approach of the N—H hydrogen to the carbonyl group.

While the conformation around the C—N bond is always well defined, that around the C$=$O is not and worthy of some comments. It has been shown from crystal data that there is a statistically significant tendency for the hydrogen bond to be located along the lone-pair directions of the carbonyl oxygen (Murray-Rust & Glusker, 1984). This ideal situation corresponds to θ = 120° and θ-tors = 0° for a perfect *SYN* conformation or $\pm 180°$ for a perfect *ANTI* conformation. For N—H$\cdots$O$=$C hydrogen-bonded compounds, in particular, Taylor *et al.* (1983) have found that the maximum proton occurrence is within 13° from the lone-pair plane (as defined by θ-tors) and at a θ value which is $\sim$10° greater than the idealized sp^2 lone-pair direction. By means of semiempirical and *ab initio* calculations on formamide and N-methylacetamide, Adalsteinsson *et al.* (1996) have identified similarly located zones of minimun energy though protected by a very low energy barrier

Table 3. *Selected bond lengths (Å) with e.s.d.'s in parentheses*

Compound	C1—O1	C1—C2	C2—C3	C3—N1	N1—C(phenyl/alkyl)
(1)	1.241 (2)	1.415 (3)	1.370 (2)	1.352 (2)	1.415 (2)
(2)	1.242 (3)	1.413 (3)	1.362 (3)	1.342 (3)	1.426 (3)
(3)	1.240 (3)	1.408 (3)	1.362 (3)	1.345 (3)	1.416 (3)
(4)	1.240 (2)	1.436 (2)	1.373 (2)	1.353 (2)	1.431 (2)
(5)	1.246 (4)	1.414 (5)	1.364 (5)	1.343 (4)	1.429 (4)
(6)	1.241 (2)	1.404 (2)	1.370 (2)	1.331 (2)	1.452 (2)
(7)	1.239 (2)	1.425 (2)	1.366 (2)	1.348 (2)	1.421 (2)
(8A)	1.229 (3)	1.423 (4)	1.357 (3)	1.349 (3)	1.414 (3)
(8B)	1.233 (3)	1.417 (3)	1.359 (3)	1.363 (3)	1.409 (3)
(9)	1.243 (3)	1.410 (3)	1.368 (3)	1.326 (3)	1.452 (3)
(10A)	1.236 (3)	1.425 (3)	1.360 (3)	1.357 (3)	1.415 (3)
(10B)	1.232 (3)	1.417 (4)	1.358 (3)	1.352 (3)	1.421 (3)
(11)	1.241 (2)	1.429 (2)	1.359 (2)	1.356 (2)	1.414 (2)
(12)	1.237 (3)	1.437 (4)	1.351 (3)	1.368 (4)	1.391 (4)
(13 A)	1.238 (3)	1.415 (4)	1.354 (3)	1.349 (3)	1.408 (3)
(13B)	1.241 (3)	1.419 (4)	1.357 (3)	1.344 (3)	1.418 (4)
(14)	1.248 (3)	1.411 (4)	1.371 (4)	1.366 (3)	1.412 (4)
(15)	1.219 (3)	1.425 (3)	1.355 (4)	1.347 (3)	1.418 (3)

Fig. 2. *ORTEP* (Johnson, 1976) views of the molecules with thermal ellipsoids at 30% probability and their hydrogen-bonded catemer motifs.
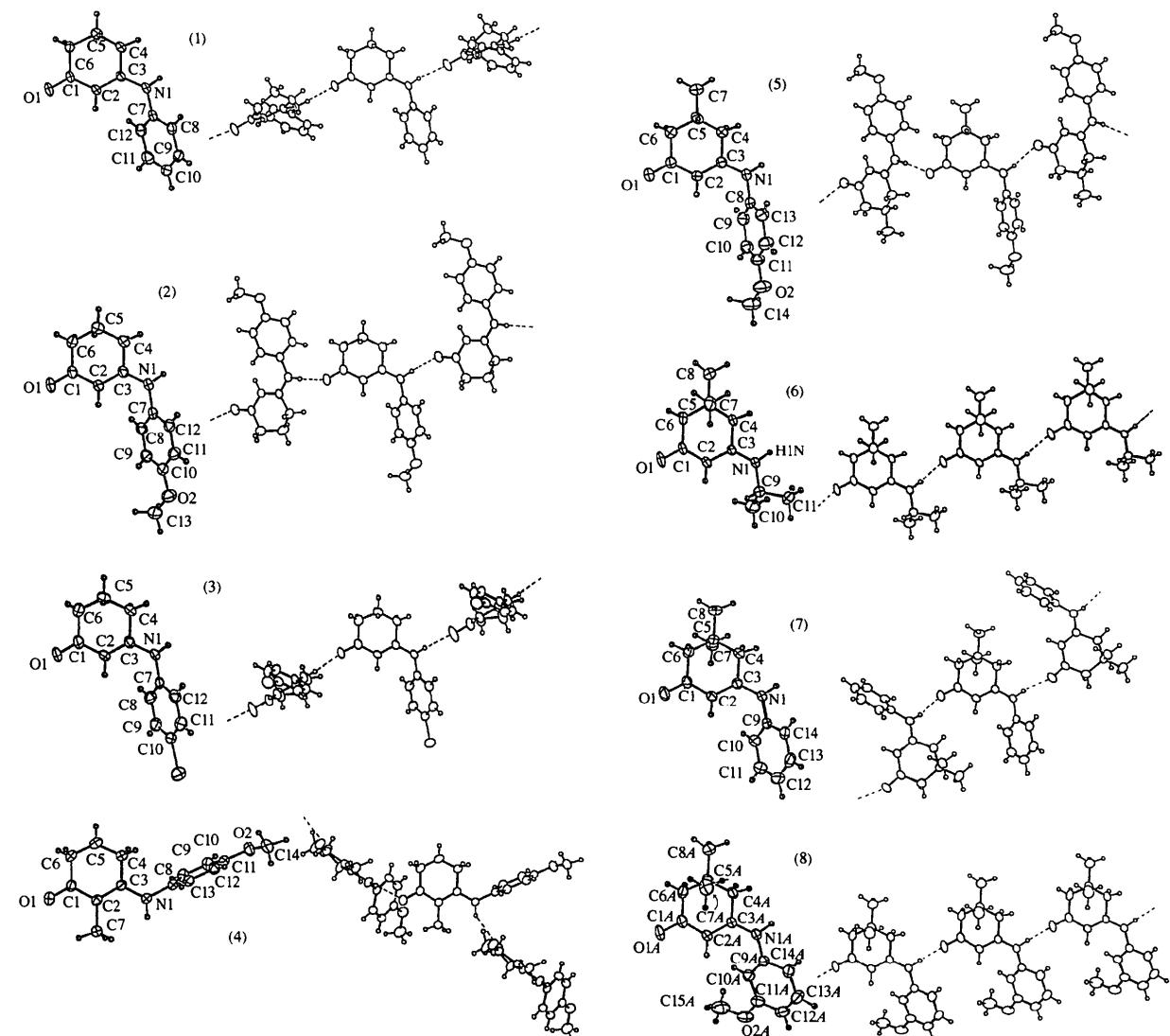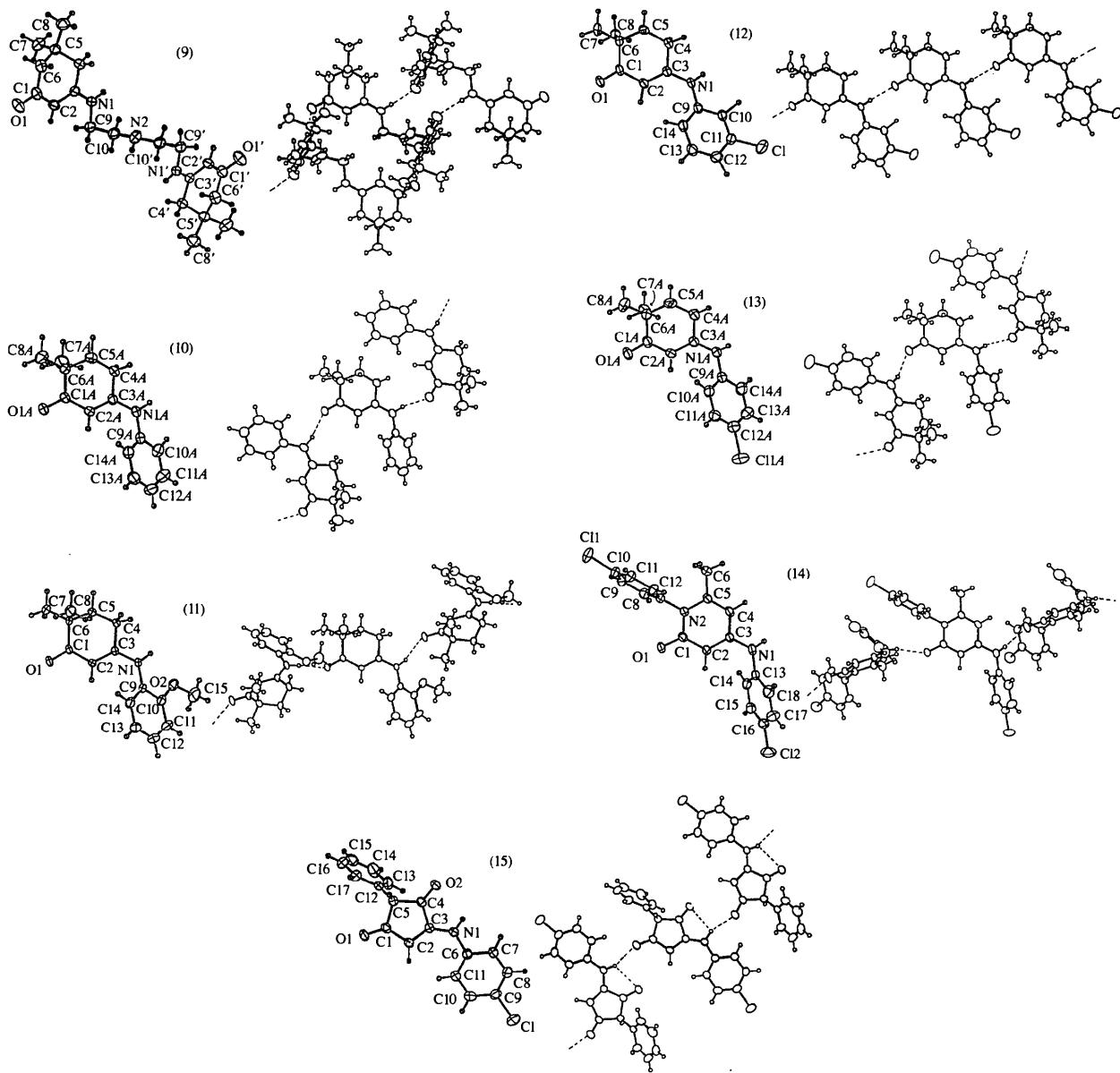
Fig. 2. (cont.)

(~0.4 kJ mol^{-1}). Present results (Table 5) show that the θ angle assumes values in the lone-pair range (say, 120–160°) in 12 out of 18 cases, but that it is larger than 160° in 1 out of 3 cases. This location of the proton outside the lone-pair direction, which has been called here LINEAR, is not observed in the analogous family of β-diketone enols and can be imputed to the fact that the N—H· · ·O bond in simple enaminones is rather weaker than the corresponding O—H· · ·O bond in β-diketones, and then is unable to orient the proton in the direction of maximum overlap with the lone-pair electron density. In the case of linearity, both φ-tors and θ-tors angles lose their meaning and have been indicated by the symbol n.d.

(not defined) in Table 5. Even when θ-tors is in the lone-pair range, however, the localization of the proton on the carbonyl plane is rather loose, clustering within 28±12° from the exact SYN or ANTI locations.

Understanding chain motifs is believed to be an important goal of crystal engineering because it would allow us to predict and control the self-assembly of molecules. Although present hydrogen-bonded chains display some similarities in the isostructural pairs (2)/(5) and (10)/(13), the rather large number of arrangements observed are too difficult to be easily rationalized. The main unifying factor derives from the fact, commonly oberved in most organic crystals, that only a limited

Table 4. *Hydrogen-bonding parameters (Å,°) with e.s.d.'s in parentheses*

D—H···A	D—H	D···A	H···A	D—H···A
(1)				
N1—H1N···O1^i	0.85 (2)	2.851 (1)	2.04 (2)	167 (2)
(2)				
N1—H1N···O1^{ii}	0.88 (2)	2.852 (2)	1.97 (2)	174 (2)
(3)				
N1—H1N···O1^{iii}	0.80 (2)	2.825 (3)	2.04 (2)	167 (2)
(4)				
N1—H1N···O1^{iv}	0.87 (2)	2.989 (2)	2.19 (2)	151 (1)
(5)				
N1—H1N···O1^v	0.86 (3)	2.914 (4)	2.06 (3)	173 (2)
(6)				
N1—H1N···O1^{vi}	0.85 (1)	2.872 (1)	2.03 (1)	174 (1)
(7)				
N1—H1N···O1^{vii}	0.85 (2)	2.859 (2)	2.02 (2)	168 (1)
(8)				
N1*A*—H1N*A*···O1*A*^{viii}	0.90 (2)	2.757 (3)	1.86 (2)	173 (2)
N1*B*—H1N*B*···O1*B*^{ix}	0.82	2.797 (3)	1.99 (2)	174 (2)
(9)				
N1—H1N···O1^x	0.82 (2)	2.843 (3)	2.04 (2)	167 (2)
(10)				
N1*A*—H1N*A*···O1	0.87 (2)	2.839 (3)	1.99 (2)	164 (2)
N1*B*—H1N*B*···O1*A*^{xi}	0.91 (2)	2.869 (3)	1.97 (2)	167 (2)
(11)				
N1—H1N···O1^{xii}	0.87 (2)	2.967 (2)	2.12 (2)	167 (2)
(12)				
N1—H1N···O1^{vi}	0.78 (2)	2.893 (3)	2.12 (2)	169 (2)
(13)				
N1*A*—H1N*A*···O1*B*^{xi}	0.76 (2)	2.841 (3)	2.11 (2)	164 (2)
(14)				
N1—H1N···O1^{xiii}	0.77 (2)	2.950 (3)	2.20 (2)	169 (2)
(15)				
N1—H1N···O1^{xiv}	0.87 (3)	2.934 (3)	2.12 (3)	157 (2)
N1—H1N···O2	0.87 (3)	2.790 (3)	2.38 (2)	110 (2)

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x, -y - \frac{1}{2}, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $-x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $x + 1$, y, z; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$; (viii) $x, y + 1, z$; (ix) $x, y - 1, z$; (x) $x, -y, z - \frac{1}{2}$; (xi) $x, y, z - 1$; (xii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (xiii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (xiv) $-x - \frac{1}{2}, y + \frac{1}{2}, -z$.

number of symmetry operations are able to produce the catemer motif, *i.e.* the screw axis 2_1, the glide g and the simple translation t, because the remaining cases of double asymmetric unit [(10) and (13)] are reducible to pseudo-2_1 chains.

Chains of 2_1 symmetry consist of ribbons which are only moderately crinkled (φ-plane = 25±9°) with *anti-ANTI* or *anti-SYN* conformations. This last geometry seems to be favored by 5- or 6-substitution on the 3-amino-2-cyclohexen-1-one fragment. The shape and elongation of the chain appear to be mainly governed by θ-tors, *i.e.* the C—C=O···H torsion angle, as exemplified by (2), (7) and (10) of Fig. 4. When θ-tors = *ac* [as in the *ac-anti-ANTI* chain of (2)], the enaminone fragments make an elongated zigzag motif characterized by a long chain pitch [7.024 Å in (2)] and scalloped edges which stick into two adjacent chains by intermolecular van der Waals interactions. When, however, θ-tors becomes smaller [as in the *sc-anti-SYN* chain of (7) and more so in the *sp-anti-SYN* chain of (10)], chained molecules bend into themselves and link by intramolecular van der Waals forces acting parallel to the

hydrogen-bonded chain. These chains have shorter translation periods [6.530 Å in (7) and 6.048 Å in (10)] and appear to pack among themselves in a looser way, as shown by the values of the calculated densities which are 1.23, 1.16 and 1.16 g cm^{-3} in (2), (7) and (10), respectively.

The different g-catemer motifs are represented in Fig. 5. The chain is roof-shaped with almost perpendicular adjacent enaminone fragments, φ-plane values being mostly in the range 78–85° with the only exception being (11), where this angle is only 48.4°. It is interesting to remark that analogous g chains formed by the homologous ···O=C—C=C—OH··· enolone groups are normally strictly planar with φ-plane angles of a few degrees (Gilli *et al.*, 1993; Bertolasi *et al.*, 1996). This different behavior can be imputed to the lower steric hindrances of —OH with respect to the —NHR group. All compounds with *anti-ANTI* and *anti-LINEAR* conformations produce extended chains with translational components in the range 7.102–7.214 Å, exemplified in Fig. 5 by (1) and (11). Compound (9) in the *sc-anti-SYN* conformation displays a very short translational compo-

Table 5. *Summary of hydrogen-bonded chain parameters (Å,°) in crystals of (1)–(15) (symbols are explained in the text)*

| Compound	Space group	Symmetry operation	Chain morphology	Chain translation	φ-plane	φ-tors CNOC	θ-tors CCOH	θ C=OH	N···O	α N—H—O	ν(N—H) (cm⁻¹)
(2)	$P2_1/n$	2_1	ac-anti-ANTI	$b/2 = 7.024$	49.0 (3)	−133.1 (2)	−104.6 (9)	136.9 (6)	2.852 (2)	174 (2)	3116
(5)	$P2_1/n$	2_1	ac-anti-ANTI	$b/2 = 6.834$	39.5 (1)	137.3 (3)	−146.5 (9)	121.1 (8)	2.914 (4)	173 (2)	3212
(7)	$P2_1/a$	2_1	sc-anti-SYN	$b/2 = 6.530$	17.1 (1)	−63.6 (3)	56.7 (9)	152.9 (4)	2.859 (2)	168 (1)	3237
(15)	$P2_1/a$	2_1	sp-anti-SYN	$b/2 = 6.666$	12.6 (2)	−8.5 (6)	9 (2)	154.5 (7)	2.934 (3)	157 (2)	3239
(10A)	$P\bar{1}$	$t(A{-}B)$ /pseudo-2_1	sp-anti-SYN	$c/2 = 6.048$	20.9 (2)	−13.2 (4)	14 (1)	142.2 (7)	2.839 (2)	164 (2)	3239
(10B)	$P\bar{1}$	$t(B{-}A)$/ pseudo-2_1	sp-anti-SYN	$c/2 = 6.048$	20.9 (2)	−15.3 (4)	19 (1)	143.1 (7)	2.869 (3)	167 (2)	3239
(13A)	$P\bar{1}$	$t(A{-}B)$/ pseudo-2_1	sp-anti-SYN	$c/2 = 6.022$	28.1 (2)	−22.0 (4)	27.2 (9)	140.6 (6)	2.841 (3)	164 (2)	3231
(13B)	$P\bar{1}$	$t(B{-}A)$/ pseudo-2_1	sp-anti-SYN	$c/2 = 6.022$	28.1 (2)	−21.2 (4)	27.7 (9)	139.0 (6)	2.850 (3)	162 (2)	3231
(14)	Pbca	g	ac-anti-ANTI	$a/2 = 7.122$	78.1 (2)	−137.8 (4)	−155 (1)	144.7 (6)	2.950 (3)	169 (2)	3239
(11)	Pbca	g	ap-anti-ANTI	$b/2 = 7.102$	48.4 (2)	155.1 (2)	154.1 (8)	141.3 (5)	2.967 (2)	167 (2)	3260
(1)	$P2_1/c$	g	n.d.-anti-LINEAR	$c/2 = 7.214$	79.5 (2)	n.d.	n.d.	175.1 (5)	2.851 (2)	167 (2)	3264
(3)	$P2_1/c$	g	n.d.-anti-LINEAR	$c/2 = 7.029$	84.4 (2)	n.d.	n.d.	169.8 (6)	2.825 (3)	167 (2)	3250
(9)	C2/c	g	sc-anti-SYN	$c/2 = 5.667$	82.7 (2)	62.3 (3)	29.2 (7)	123.0 (6)	2.843 (3)	167 (2)	3221
(4)	$P2_1/n$	g	ac-syn-ANTI	$n/2 = 6.491$	83.8 (1)	100.1 (2)	151.5 (6)	120.0 (5)	2.989 (2)	151 (2)	3250
(6)	$P\bar{1}$	t	n.d.-anti-LINEAR	$a = 7.139$	0	n.d.	n.d.	165.4 (4)	2.872 (1)	174 (1)	3266
(8A)	Pna2₁	$t(A{-}A)$	n.d.-anti-LINEAR	$b = 7.180$	0	n.d.	n.d.	174.2 (8)	2.757 (3)	173 (2)	3258
(8B)	Pna2₁	$t(B{-}B)$	n.d.-anti-LINEAR	$b = 7.180$	0	n.d.	n.d.	167.7 (8)	2.797 (3)	174 (2)	3258
(12)	$P2_1$	t	n.d.-anti-LINEAR	$a = 7.313$	0	n.d.	n.d.	163.6 (7)	2.893 (3)	169 (2)	3293
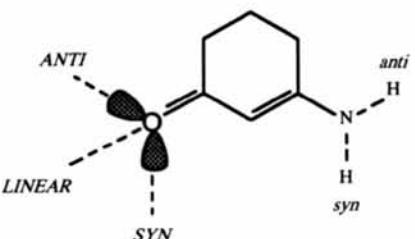
Fig. 3. The *syn/anti-SYN/ANTI/LINEAR* stereochemical nomenclature for the description of chain conformations.

(2): *ac-anti-ANTI*   (7): *sc-anti-SYN*

(10): *sp-anti-SYN*
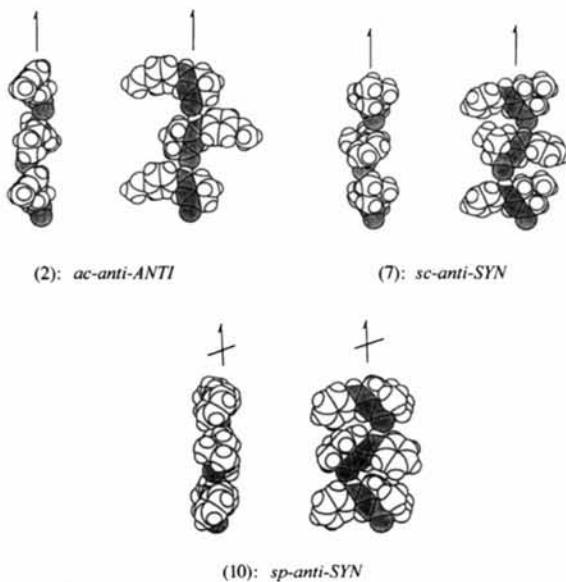
Fig. 4. The 2_1 (or pseudo-2_1) chain arrangements projected on two mutually perpendicular planes, displayed by (2), (7) and (10). The shading indicates the O=C—C=C—N enaminone fragment.


(11): *ap-anti-ANTI*   (1): n.d.-*anti-LINEAR*

(9): *sc-anti-SYN*   (4): *ac-anti-ANTI*
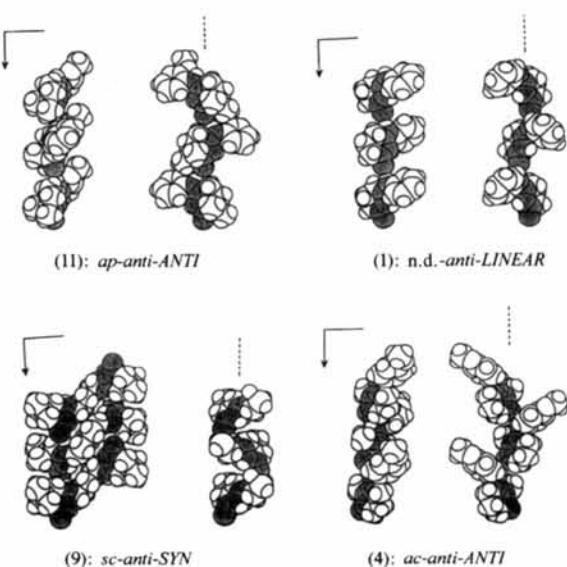
Fig. 5. The *g* chain arrangements projected on two mutually perpendicular planes, displayed by (11), (1), (9) and (4). The shading indicates the O=C—C=C—N enaminone fragment.

Table 6. *Intermolecular N···O hydrogen-bond distances and C=O bond distances (Å) for simple enaminones of Fig. 6*

Compound	Refcode	$d(N···O)$	$d(C=O)$	Reference
(IVa)	ANPRAL	2.801	1.233	(a)
(IVb)	BECWAH	2.900	1.234	(b)
(IVc)	DIGGEF	2.873	1.239	(c)
(V)	ANTHOA	2.906	1.232	(d)
(VIa)	PEBVUN01	2.931	1.244	(e)
(VIb)	ZAMVEO	2.857	1.243	(f)
(VIIa)	JAZDOD	2.829	1.242	(g)
(VIIb)	WIJZEU	2.787	1.239	(h)

(a) Kulpe & Schulz (1979); (b) Kessler *et al.* (1981); (c) Reichardt *et al.* (1985); (d) Skinnemoen & Ottersen (1980); (e) Kubicki & Codding (1993); (f) Huang *et al.* (1995); (g) Rodriguez *et al.* (1989); (h) Ianelli *et al.* (1994).


(8): n.d.-*anti-LINEAR*
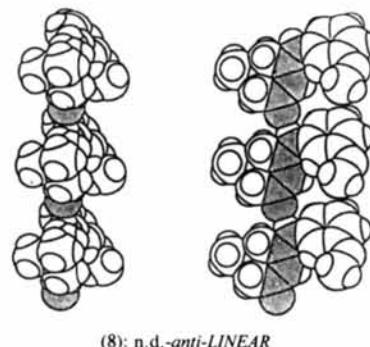
Fig. 6. The *t* chain arrangement projected on two mutually perpendicular planes, displayed by (8). The shading indicates the O=C—C=C—N enaminone fragment.

(IVa): R_1 = H; R_2 = H; R_3 = Ph
(IVb): R_1 = cyclohexane; R_2 = H; R_3 = Me
(IVc): R_1 = H; R_2 = 2,4,6-cycloheptatrien-1-yl;
          R_3 = Ph

(V)

(VIa): R_1 = Me; R_2 = -COOMe;
          R_3 = -CH$_2$-Ph
(VIb): R_1 = H; R_2 = H; R_3 = *m*-NO$_2$-Ph


(VIIa): R = H
(VIIb): R = Me
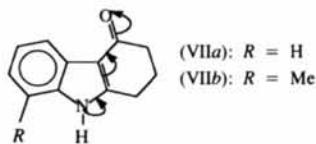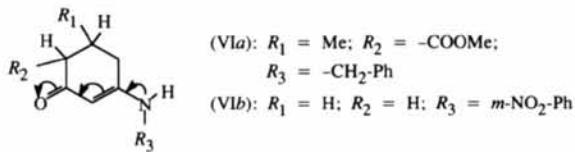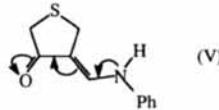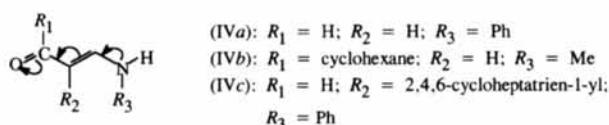
Fig. 7. Chemical formulae of simple secondary enaminones retrieved from the literature.

nent of 5.667 Å, probably due to the cooperative effect of the two hydrogen-bonded chains interconnected by the azapentane group. Compound (4) is characterized by the unique *ac-syn-ANTI* chain arrangement, determined by the steric hindrance of the methyl group in position 2, and displays a translational component along the *ac* cell diagonal of 6.491 Å.

Simple translational *t* chains, represented by (8) in Fig. 6, are essentially ribbons of parallely arranged molecules (φ-plane = 0°) with n.d.-*anti-LINEAR* conformations, where the hydrogen bond is not oriented along the oxygen lone-pair direction, but forms large C=O$\cdots$H angles of 164–174°. Such a linearity leads to elongated chains (chain translations of 7.139–7.313 Å) even in the case of remarkably short hydrogen bonding [see for instance (8) with a N$\cdots$O distance of 2.777 Å, on average].

The chaining of enaminone groups by means of intermolecular N—H$\cdots$O=C RAHBs is thus the dominating feature of the crystal packing, the chain

Table 7. *Short intermolecular* N$\cdots$O *hydrogen-bond distances and* C=O *bond distances for enaminones of Fig. 7*

Compound	Refcode	d(N$\cdots$O)	d(C=O)	Reference
(VIIIa)	MCHYPY10	2.753	1.252	(a)
(VIIIb)	SAVYAP	2.705	1.268	(b)
(VIIIc)	GALDAY	2.796	1.280	(c)
(IXa)	HIBHOP	2.750	1.285	(d)
(IXb)	HIBHUV	2.732	1.275	(d)
(IXc)	HIBJAD	2.649	1.255	(d)
(IXd)	FETSEC	2.716	1.256	(e)
(X)	ZZZGEO01	2.786	1.236	(f)
(XI)	AMTURM01	2.730	1.252	(g)
(XIIa)	DEBFAR02	2.673	1.247	(h)
(XIIb)	KUBVOS	2.789	1.251	(i)
(XIIc)	MPYAZO10	2.627	1.284	(j)
(XIId)	ZILJIN	2.733	1.245	(k)
(XIIIa)	COVLII	2.694	1.252	(l)
(XIIIb)	COVLOO	2.766	1.250	(l)
(XIIIc)	JEHJAH	2.750	1.265	(m)
(XIIId)	JEPPAV	2.722	1.256	(n)
(XIIIe)	VEJRIL	2.718	1.246	(o)

(a) Boer (1972); (b) Bradshaw *et al.* (1987); (c) Nelson *et al.* (1988); (d) Toledo *et al.* (1994); (e) Lowe *et al.* (1987); (f) Delange *et al.* (1986);(g) Raper *et al.* (1985); (h) Akama *et al.* (1995); (i) Sieler *et al.* (1992); (j) De Camp & Stewart (1971); (k) Bertolasi *et al.* (1995); (l) Ferretti *et al.* (1985); (m) Shiro (1990); (n) Nakai (1990b); (o) Nakai (1990a).

translational component determining the length of one of the cell parameters. In all crystals studied the infinite chains are antidromically arranged, showing that the molecular dipole generated by the π-delocalization of the enaminone system is a second essential factor of the crystal packing. Accordingly, no polar crystals containing a unique system of homodromic chains have been observed. Also in (8) and (12), which crystallize in the polar space groups $Pna2_1$ and $P2_1$, antidromic chains of simple translation perpendicular to the 2_1 axis are preferred to the homodromic polar chain parallel to it. Since enaminone chaining dominates the packing, the enaminone group itself can be defined as a supramolecular synthon according to Desiraju (1995), which is deputed, in this specific case, to form antiparallel chains of molecules linked by resonant-assisted hydrogen bonds.

3.2. Hydrogen-bond strength

To discuss hydrogen-bond strength, the most relevant parameters are the N$\cdots$O contact distance and the C=O bond distance, the latter being an indicator of increased delocalization of the π-conjugated system induced by RAHB. In present structures of simple (*i.e.* not substituted by heteroatoms) secondary enaminones [(1)–(13)] average values of $<d$(N$\cdots$O)$>$ = 2.86 ± 0.06 and $<d$(C=O)$>$ = 1.239 ± 0.004 Å are found. Similar results are obtained for the few simple enaminones retrievable from CSD files (Table 6, Fig. 7), for which $<d$(N$\cdots$O)$>$ = 2.86 ± 0.05 and $<d$(C=O)$>$ =

(VIIIa): R_1 = Cl; R_2 = Me; R_3 = Me; R_4 = Cl
(VIIIb): R_2–R_3 = crown ether
(VIIIc): R_1 = OH; R_2 = Me

(IXa): R_1 = H; R_2 = *p*-Cl-Ph; X = CH
(IXb): R_1 = H; R_2 = *p*-OMe-Ph; X = CH
(IXc): R_1 = CN; R_1 = Me; X = CH
(IXd): R_1 = H; R_2 = Me; X = N

(XIIa): R_1 = Ph; R_2 = Me; R_3 = -C(O)Ph
(XIIb): R_1 = 2-pyridyl; R_2 = Me; R_3 = H
(XIIc): R_1 = H; R_2 = Me, R_3 = H
(XIId): R_1 = Ph; R_2 = H; R_3 = 3-Me-1-phenylpyrazol-5-yl

(XIIIa): R = Ph
(XIIIb): R = *p*-Cl-Ph
(XIIIc): R = 5-methylthien-2-yl
(XIIId): R = 5-methylthien-3-yl
(XIIIe): R = 4-methylthien-2-yl

Fig. 8. Chemical formulae of substituted secondary enaminones displaying shorter N$\cdots$O intermolecular hydrogen-bond distances retrieved from the literature.

Table 8. *Summary of average* N$\cdots$O *and* C$=$O *distances and corresponding variability ranges (Å) for* N—H$\cdots$O *hydrogen bonds among compounds of different classes*

Class of compounds	n	d(N$\cdots$O)		d(C$=$O)		Reference
		Range	Average	Range	Average	
Nonresonant	27	2.87–3.29	3.08 ± 0.14	1.20–1.23	1.214 ± 0.014	†
Secondary simple amides	36	2.81–2.97	2.89 ± 0.04	1.22–1.25	1.234 ± 0.009	†
Secondary simple enaminones	24	2.76–2.99	2.86 ± 0.05	1.23–1.25	1.239 ± 0.004	Tables 4 and 6
Substituted enaminones	18	2.63–2.80	2.73 ± 0.04	1.24–1.28	1.259 ± 0.014	Table 7

† See supplementary material.

1.238 ± 0.004 Å. These values are to be compared with the corresponding ones found in chains of simple secondary amides O$=$C(R)N(R')H (R and R' being aryl or alkyl groups), *i.e.* $<d$(N$\cdots$O)$>$ = 2.89 ± 0.04 Å and $<d$(C$=$O)$>$ = 1.23 ± 0.01 Å, according to a previous selection of 36 secondary amide structures reported by Gavezzotti & Filippini (1994), and in 27 CSD retrieved nonresonant $(Csp^3)_2$N—H$\cdots$O$=$C$(Csp^3)_2$ intermolecular hydrogen bonds, for which $<d$(N$\cdots$O)$>$ = ·3.08 ± 0.14 and $<d$(C$=$O)$>$ = 1.214 ± 0.011 Å. Note that all the distance averages given above refer to nonbifurcated hydrogen bonds because it is known (Taylor *et al.*, 1984) that bifurcation produces weaker, and then not comparable, hydrogen bonds. A good example of this is given by the structure of (15) which displays, besides the intermolecular N—H$\cdots$O$=$C bond, a bifurcated intramolecular one with consequent weakening of both N—H$\cdots$O bonds. Moreover, in agreement with the RAHB model, the long intermolecular N$\cdots$O distance of 2.934 (3) Å is associated with a short C$=$O distance of 1.219 (3) Å, showing a reduction of the π-delocalization along the heterodienic group.

It can be concluded that, as far as the intermolecular N—H$\cdots$O hydrogen-bond distance and the delocalization of the π-conjugated system are concerned, simple enaminones do not appear to produce hydrogen bonds stronger than amides and, by comparison of these two systems with the nonresonant one, the effect of RAHB is seen to be rather weak, only being able to shorten the N$\cdots$O average distance from 3.08 ± 0.14 to 2.86 ± 0.05 Å with a concomitant small lengthening of d(C$=$O) from 1.214 ± 0.014 to 1.239 ± 0.004 Å. Secondary enaminones, however, are functional groups which can carry substituents at the C and N atoms able to affect the π-conjugation within the heterodienic moiety and, accordingly, the resonance-controlled intermolecular hydrogen-bond strength. By searching the CSD files, it is, in fact, possible to identify a number of molecules which contain the secondary enaminone fragment, but display remarkably stronger intermolecular N—H$\cdots$O bonds with N$\cdots$O distances as short as 2.627 Å. The most significant of these are shown in Fig. 8 and their N$\cdots$O distances listed in Table 7. In the 4(1H)pyridone derivatives (VIIIa)–(c) both C$=$O and NH groups are embedded in a double heterodienic π-conjugated system and the consequent enhancement of the π-polarizability is, most probably, the reason for the

observed shortening of the N$\cdots$O distances into the range 2.705–2.796 Å. A similar effect can be expected in the 2-amino-4(1H)pyridone or -pyrimidinone derivatives (IXa)–(d), where, moreover, the 2-amino substituent adds a third π-conjugated system which can induce a further shortening of the hydrogen bond [2.649 ≤ d(N$\cdots$O) ≤ 2.750 Å]. In 6-methyl-2-thiouracil (X) and 6-amino-2-thiouracil (XI) the normal π-conjugation within the enaminone system is joined with further conjugation of the thioamidic group which, by increasing the positive and negative charges on N—H and C$=$O groups, respectively, induce an additional shortening of the hydrogen bonds [2.730 ≤ d(N$\cdots$O) ≤ 2.786 Å]. In general, the type of substitution which seems suited to produce the greatest strengthening of the intermolecular hydrogen bond among resonant secondary enaminone fragments appears to be the transformation of the carbonyl in an amidic function. Such substitution is found in (X) and (XI) as well as in the remaining classes of Table 7 and Fig. 8, that is pyrazolin-5-ones (XIIa)–(d) [2.627 ≤ d(N$\cdots$O) ≤ 2.789 Å] and (3H)-pyrazolo(4,3-c)quinolin-3-ones (XIIIa)–(e) [2.694 ≤ d(N$\cdots$O) ≤ 2.766 Å]. It has to be noticed that, although this condition seems necessary to shorten the intermolecular N$\cdots$O distance, it is by no means sufficient, as shown by (14), which, in spite of displaying the amidic group on the pyridone ring and a lengthened C$=$O bond distance (1.248 Å), shows a N$\cdots$O hydrogen-bond distance of 2.950 (3) Å, which is even longer than the average value for simple enaminones. This lengthening is probably due to unfavorable van der Waals intermolecular interactions among substituents occurring in the crystal packing.

Table 8 summarizes the N$\cdots$O and C$=$O distances for all the classes of compounds discussed in the present paper. The data collected are in agreement with the hypothesis (Bertolasi *et al.*, 1995) that the strengthening of the neutral N(R^2)H$\cdots$O$=$C hydrogen bond increases with increasing delocalization of the interleaving π-conjugated system, thus supporting the idea that RAHB (Gilli *et al.*, 1989; Gilli *et al.*, 1996) is also effective in heteronuclear hydrogen bonds, although in this case the effect of the substituents is more difficult to be generalized.

Italian Service for Diffusion of Crystallographic Data (CNR, Parma) for access to CSD files.

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